Novel Photonic Crystals: Incorporation of Nano-CdS into the Natural Photonic Crystals within Peacock Feathers

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In this investigation, the natural 2D photonic crystals (PhCs) within peacock feathers are applied to incorporate CdS nanocrystallites. Peacock feathers are activated by ethylenediaminetetraacetic/dimethylformamide suspension to increase the reactive sites on the keratin component, on which CdS nanoparticles (nano-CdS) are in situ formed in succession and serve as the "seeds" to direct further incorporation during the following solvothermal procedure. Thus, homogeneous nano-CdS are loaded both on the feathers' surface layer and inside the 2D PhCs. The obtained nano-CdS/peacock feathers hybrids are novel photonic crystals whose photonic stop bands are markedly different from that of the natural PhCs within original peacock feathers, as observed by the reflection spectra.

Introduction

The composites constructed by photonic crystals (PhCs) and infiltrated light emitting species are promising materials in both solid-state physics and modern photonic devices, since the spontaneous light emission from the infiltrated species is supposed to be modified at specific wavelength and specific directions by the PhCs structure.[1,2] According to the formation stage of PhCs as the hybridization happens, the fabrication routes to such systems could be divided into three types: (a) the infiltration of preformed[3,4] or in situ synthesized[5,6] light-emitting species into ready PhCs; (b) the in situ synthesis of quantum dots (QD) on the building blocks of PhCs (microspheres);[7] (c) the hierarchical self-assembly that QD hybridize with the molecule components of the microspheres.[8,9]

The above-mentioned systems are mainly based on the artificial PhCs with (nearly) close-packed patterns assembled by colloidal polymers[7−9] or silica spheres,[3,6] while other patterns require highly expensive equipment and sophisticated processes.[4,5] The pattern limitation of low-cost artificial PhCs might be an obstacle to the investigation and application of QD infiltrated PhCs. Actually, natural PhCs with various patterns[10] are hopeful substrates for the embedment of QD to create valuable properties and wider applications. And peacock feathers are likely to be the good candidates. As reported by Yoshioka et al.[11] and Zi et al.,[12,13] they contain 2D photonic crystal structures beneath their surface keratin layers, which are composed of arrays of melanin rods connected by keratin. By variation of the lattice constant and period number, peacock feathers provide several 2D photonic crystal structures that control the visible light propagation to display different iridescent colors.

Concerning light emitting species, CdS is a typical II−VI semiconductor that has a direct bandgap near 2.4 eV for bulk material.[14] CdS nanoparticles (nano-CdS) display controllable photoluminescence that spans the visible spectrum by tuning the size[15] and surface functionality.[16] Thus, the incorporation of nano-CdS into PhCs might realize highly tunable spontaneous emission within a single structure, which is essential to create nanoscaled light sources.[9] Moreover, it is observed that synthetic PhCs have some influence on the spontaneous emission from the incorporated nano-CdS.[6,17] Since peacock feathers have the ability to control visible light, it should also be valuable to integrate nano-CdS into the natural PhCs within peacock feathers.

Recently, an in situ process has been carried out to embed nano-ZnO (ZnO nanoparticles) into peacock feathers in our group.[18] Although the embedment is achieved, the loading of QD is relatively low so that the reflection spectra of peacock feathers remain intact after the process. The low loading might be due to the limited reactive sites and the finite nucleation on original peacock feathers. Inspired by the acylation of wool keratin fibers with ethylenediaminetetraacetic (EDTA) dianhydride to enhance the keratin's metal uptake,[19,20] it is hopeful that using EDTA to arouse more reactive sites on the keratin of peacock

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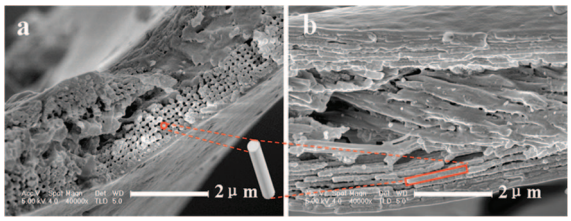

Figure 1. FESEM images of the (a) transverse and (b) longitudinal cross section of a barbule on the red barb, revealing the ordered arrays of keratin-coated melanin rods beneath the feather surface.

feathers for the efficient loading of nano-CdS. In addition, dimethylformamide (DMF) can fully infiltrate into peacock feathers without lotus effect and with keratin unspoiled;[21] thus it may be befitting to be chosen as the assistant medium for the EDTA activation. Besides, the introduction of a solvothermal process might be useful to further achieve the loading of QD on the keratin component. Hereby, natural peacock feathers are activated by EDTA/DMF treatment and then introduced to a two-step soakage procedure that include preloading and solvothermal loading to efficiently incorporate nano-CdS into the 2D PhCs within peacock feathers, finally resulting in novel photonic crystals.

Experimental Section

Peacock has several kinds of feathers with different colors. The barbs from the eye region of the tail feathers and from the body covering have been intensively investigated by Yoshioka et al.[11] and Zi et al.,[12,13] and various colors correspond to the 2D PhCs with different parameters. Below the eye region, there are abundant red barbs loosely arranged along the white tail stem. The scanning electron microscopy (SEM) images of the red barb clearly show the ordered arrays (Figure 1a) and rod features (Figure 1b) of the keratin-coated melanin rods beneath the surface keratin. Thus, the red barb also contains the 2D photonic crystal structure (lattice constant: 137 nm), which is similar to the observation by Yoshioka et al.[11] and Zi et al.[12,13] In this investigation, both the red barbs and the barbs from the eye region are involved.

Original peacock feathers were openly immersed in EDTA/DMF (about 1:10 v/v) suspension at 110 °C for several hours to obtain EDTA/DMF activated feathers (mentioned as E/D-feathers). The ED–feathers were soaked in $CdCl_2$ solution (containing 0.4 g of $CdCl_2 \cdot 2.5H_2O$, 5 mL ethanol, and 4 mL ammonia) for 30 min, taken out and rinsed thoroughly, and then soaked in 12.5 mM Na_2S ethanol solution for 30 min and again taken out and rinsed thoroughly to obtain the "substrate feathers" (soakage 1). The substrate feathers were in succession put into the above-mentioned $CdCl_2$ solution, followed by the addition of thiourea (0.115−0.18 g), and then the system was placed in an autoclave and kept at 100 °C for 30−40 min (soakage 2). Finally, the treated feathers were taken out and rinsed thoroughly to harvest target samples.

Several control experiments were taken to investigate the process as listed in Table 1. To describe each sample, the features of the two tunable experimental stages (the activation stage and soakage 1) are summarized and connected by "−" to form the label. Sample E/D-RT is the target sample which was obtained by the typical procedure, characterizing the EDTA/DMF activation stage (E/D) and soakage 1 at room temperature (RT). Sample N-RT represents the sample that missed the activation stage (N) but kept soakage 1 at room temperature (RT). Sample D-RT stands for the sample deriving from the activation stage by DMF treatment (D) and soakage 1 at room temperature (RT). Sample N−N signs the sample that missed both the activation stage (N) and soakage 1 (N). Sample E/D-60 figures the sample from the EDTA/DMF activation stage (E/D) and soakage 1 at 60 °C (dipping in Cd^{2+} solution at 60 °C but in S^{2-} solution at room temperature). In addition, soakage 2 is the same procedure for all the 5 cases to skip over being labeled.

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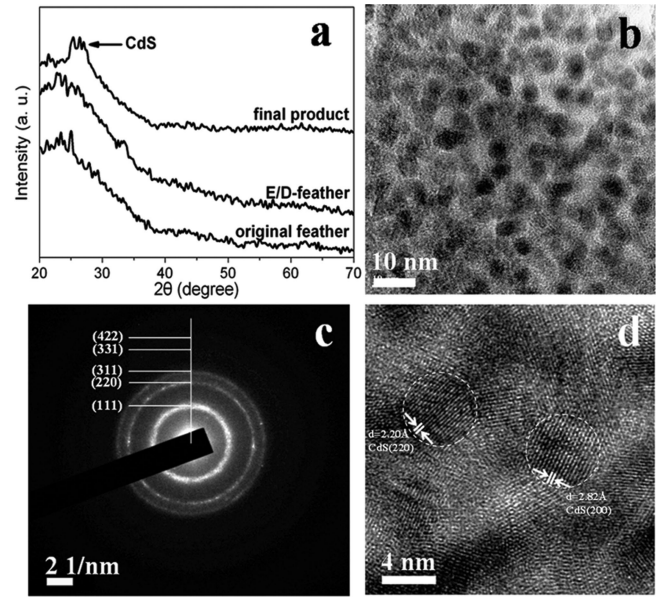

Figure 2. (a) XRD patterns of the original peacock feather, the E/D-feather, and the final product (sample E/D-RT). (b and d) HRTEM images and (c) SAED patterns of the incorporated nano-CdS, which were shaken off from the feather and dispersed in ethanol via ultrasonic agitation.

FESEM images were investigated on an FEI Sirion 200 field emission gun scanning electron microscope operated at an acceleration voltage of 5.0 kV. XRD measurements were carried out on a D/max-2550/PC instrument. HRTEM measurements were taken on a JEM-2100F instrument under an acceleration voltage of 200 kV, and both bright field images and selected area electron diffraction (SAED) were examined. FTIR measurements were recorded on a Bruker EQUINOX 55 instrument at a resolution of 0.44 cm^{-1} and in a spectral range of 2300−400 cm^{-1}. Reflection spectra were measured on a CRAIC QDI 2010 superior microspectrophotometer. Microphotographs were taken on a KEYENCE VHX 600 microscope.

Results and Discussion

Figure 2a shows the XRD patterns of the original peacock feather, the E/D-feather, and the final product. It is obvious that the immersion in EDTA/DMF suspension causes little change of the patterns, while the successive incorporation by the two-step soakage procedure increases the signal intensity around 2θ position of 27°, which could be attributed to CdS. Further investigation was carried out by ultrasonic agitation of the final product. As revealed by the HRTEM images in parts b and d of Figure 2, the particles perform nearly round spheres with diameter 5−6 nm. The corresponding SAED patterns (Figure 2c) match well with the cubic CdS structure reported in JCPDS cards 89-0440, and the relevant planes are indexed as (111), (220), (311), (331), and (422). Besides, the absence of the characteristic diffraction rings (101) and (102) of hexagonal CdS corresponding to *d* spacings 0.316 and 0.245 nm in Figure 2c suggests that the obtained CdS are all cubic phase nanocrystallites. Moreover, the HRTEM image in Figure 2d exhibits clear lattice fringes with *d* spacings 0.22 and 0.282 nm, according to the (220) and (200) reflections of cubic CdS structure, respectively. Therefore, one can draw a conclusion that cubic phase CdS nanocrystallites with diameter 5 ∼ 6 nm are integrated with peacock feathers by the two-step soakage procedure.

Table 1. Experimental Conditions and Corresponding Samples

experiment	activating agent[b]	soakage 1 temperature[c]	soakage 2 temperature, time[d]	sample	SEM results
1	EDTA/DMF(E/D-feather)	RT(25°C)	100°C,30min	E/D-RT[a]	*Figure 3, S1d, S2d*
2		RT(25°C)	100°C,30min	N-RT	*Figure S1a, S1b, S2a*
3	DMF(D-feather)	RT(25°C)	100°C,30min	D-RT	*Figure S1c*
4			100°C,30min	N-N	*Figure S2b*
5	EDTA/DMF(E/D-feather)	60 °C	100°C,30min	E/D-60	*Figure S2c*

[a] Target products. [b] The solvent to activate original feathers. [c] Preloading that dipping in Cd^{2+} solution at different temperature and S^{2-} solution at RT in turn. [d] Solvothermal process at 100 °C for 30 min

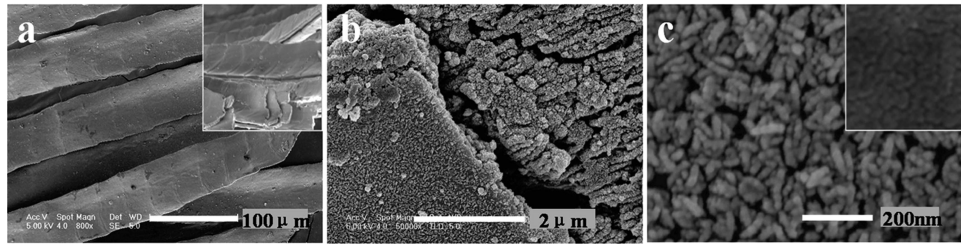

Figure 3. FESEM images of the nano-CdS/peacock feather hybrid (sample E/D-RT). Insets in parts a and c show the images of the original peacock feather under the corresponding magnifications.

The distribution of nano-CdS on peacock feathers was investigated by FESEM observation. As depicted in Figure 3a, the covering of nano-CdS is so homogeneous on the surface layer that the hybrid appears almost the same as the original feather under low magnification. The surface layer of the hybrid could be partially broken during the FESEM sample preparation as observed on the upright side in Figure 3b. It can be seen that both the surface layer and the beneath arrays of rods are actually rougher than the original counterparts (Figure 1b) due to the nano-CdS covering. In addition, despite the Au coating which usually makes the boundary unclear, it is still discernible in Figure 3c that nano-CdS assemble into wormlike aggregations (nano-CdS worms). Thereby, nano-CdS are well distributed both on the feather surface and inside the beneath 2D PhCs by operating the typical procedure, which includes the activation of feathers in EDTA/DMF suspension to obtain E/D-feathers, the preloading (soakage 1) that dipping E/D-feathers in Cd^{2+} and S^{2-} solution in turn at room temperature to prepare substrate feathers as well as the solvothermal loading (soakage 2) to achieve final products "nano-CdS/feathers".

FTIR measurements were taken to monitor the feather activation. Both the feather immersed in EDTA/DMF (E/D-feather) and that in DMF (D-feather) were dried and compressed into KBr pellets to investigate the FTIR spectra. In Figure 4, the curve of the original feather presents characteristic bands of protein, relating to the keratin component.[18] Regarding the feathers treated by EDTA/DMF (E/D-feather) and DMF (D-feather), the 1728 cm^{-1} band attributed to COOH (C═O stretching from COOH of aspartic and glutamic acid residues)[22] decreases, along with the appearance of the new band around 1400 cm^{-1} that attributes to COO^- symmetric stretching.[19] In addition, the intensity of the 1400 cm^{-1} band is relatively stronger in the curve of the E/D-feather, which indicates the introduction of COO^- sites to the keratin component by EDTA. Taken into consideration that the band around 1400 cm^{-1} (COO^- st) of the final product nano-CdS/feather (sample E/D-RT) is even intensified and slightly shifted to higher wavenumber as compared with that of the E/D-feather, it is reasonable to conclude that nano-CdS interact with the feather keratin by the COO^- group in the final product (most likely by the connection between Cd^{2+} and

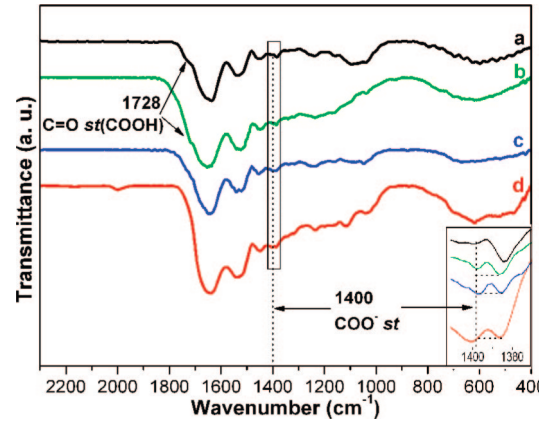

Figure 4. FTIR spectra of (a) the original feather, (b) the DMF activated feather, D-feather, (c) the EDTA/DMF activated feather, E/D-feather, and (d) the final product nano-CdS/feather, sample E/D-RT, respectively.

COO^-)[18,19] and the COO^- group should be considered as the reactive sites during the incorporation process.

Control experiments were also carried out to further investigate the influence of the activation process on the final products, as listed in Table 1 and sketched in Supporting Information. Sample E/D-RT and sample N-RT were derived from EDTA/DMF activated feathers (E/D-feathers) and unactivated feathers, respectively. As mentioned before, sample E/D-RT displays uniform covering of nano-CdS worms as shown in Figure 3c. Yet concerning sample N-RT, the covering of nano-CdS worms is inhomogeneous, and even some irregular large aggregations (diameter ~400 nm) of nano-CdS worms appear. This phenomenon reveals the efficiency of EDTA/DMF. Furthermore, by simply substituting EDTA/DMF for DMF as the activating agent, as-prepared sample D-RT also performs homogeneous covering of nano-CdS worms. However, the worms of sample D-RT are slightly larger than those of sample E/D-RT, which is also consistent with the different colors of the two samples. In a typical procedure concerning sample E/D-RT, the feathers gain additional COO^- active sites (E/D-feathers) by the effect of EDTA, which could give rise to the homogeneous distribution of nano-CdS on their keratin component, according to the above analyses of FTIR and SEM results. Thus, the amount of COO^-

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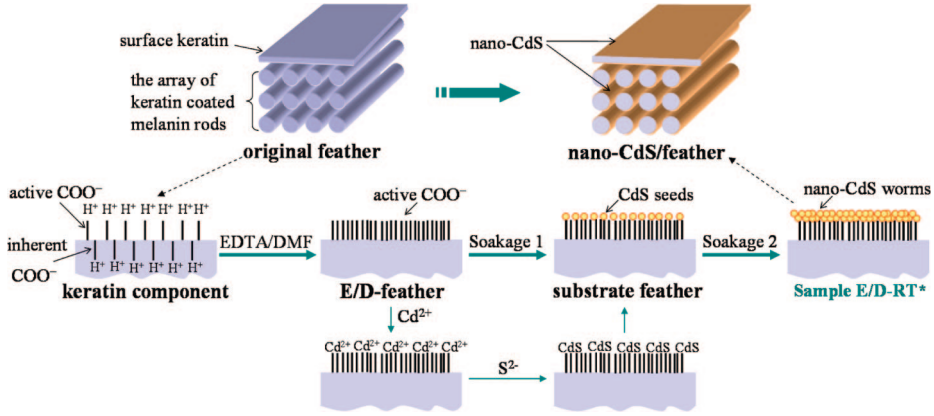
Scheme 1. Proposed Mechanism of Incorporating Nano-CdS into Peacock Feathers



active sites on the feather should be essential to control nano-CdS distribution. Moreover, the uniform nano-CdS of sample D-RT compared with that of sample N-RT could also be attributed to the larger amount of COO^- active sites on the D-feather. In contrast with EDTA, which could directly provide COO^- active sites, DMF contains no COOH group, and thereby the increased COO^- active sites on D-feather might come from the inherent COOH of the original keratin component that activated by the aid of DMF (see Figure S3 of Supporting Information). Accordingly, the COO^- active sites on the E/D-feather could be supposed to have three origins, which are the COO^- active sites on the original keratin component, the inherent COO^- sites activated by DMF, as well as the additional COO^- sites by the effect of EDTA.

The preloading soakage (soakage 1) in Cd^{2+} and S^{2-} solution in turn to prepare substrate feathers for the following solvothermal process (soakage 2) is also studied by operating control experiments. As listed in Table 1, sample N-RT was derived by soakage 1 and soakage 2, and sample N-N was prepared by only soakage 2. The preformed CdS by soakage 1 could act as "seeds" to provide the heterogeneous nucleation sites for the further incorporated nano-CdS during the solvothermal procedure; thus sample N-RT presents relatively smoother appearance than sample N-N, whose surface randomly deposits undesired large CdS aggregations and small spherical CdS ones with various diameters. Moreover, when soakage 1 happened in the Cd^{2+} solution at higher temperature (60 °C, sample E/D-60), more CdS seeds could be preformed and a larger amount of nano-CdS would nucleate on the substrate feather, that additional assemblies of nano-CdS worms (~200 nm) could coexist with the homogeneous nano-CdS layer. Therefore, it shall be crucial for the in situ reaction happening on the COO^- groups by the soakage 1 to form suitable amount of CdS seeds for the final hybrids embodied by well distributed nano-CdS.

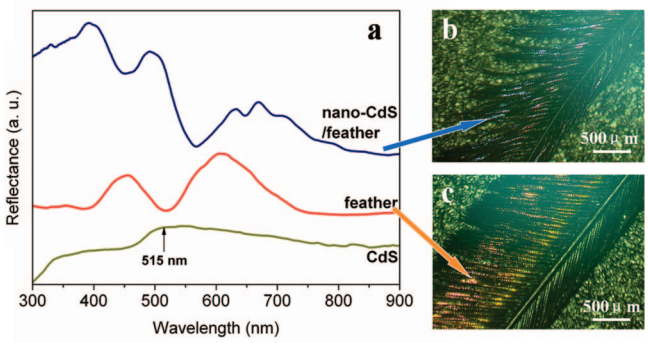


Figure 5. (a) Reflection spectra of the contrastive CdS on glass substrate, of the red barb on the original feather, and of the corresponding part on the final product nano-CdS/feather hybrid (sample E/D-RT), respectively. Microphotographs of (b) the nano-CdS/red barb hybrid and (c) the original red barb.

On the basis of the above analysis, an optimal route is established as described in Scheme 1. By the EDTA/DMF activation, the keratin component of the peacock feather (include the surface keratin and the connecting keratin in the 2D PhCs) becomes active for the further in situ reactions. During the two-step soakage, the preformed CdS by soakage 1 act as the seeds for the succedent solvothermal process (soakage 2) to finally incorporate nano-CdS homogeneously both on the feather surface and inside the 2D PhCs.

The loading of semiconductor inside PhCs to a certain degree can modify the photonic band structure that could be detected by reflection spectra.[23] Herein, related reflection spectra were collected to investigate the efficiency of loading as well as the structural information of the novel nano-CdS/feathers hybrids. As displayed in Figure 5a, the contrastive CdS obtained by the similar technique without peacock feathers (normal CdS on glass substrate) gives the reference reflection spectrum that has a step around 500 nm, corresponding to the absorption edge of CdS around 515 nm.[14] The red barb on the original feather presents a mixed structural color with two reflection peaks, which is similar to the brown part in the eye region. In addition, the 2D PhCs observed beneath the feather surface (Figure 1) are also the same type as that discussed in the reference[12,13] and should be responsible to the structural red color. Yet it is observed that the incorporation begets the change of the reflection spectrum of the feather, along with the red barb (Figure 5c) turning to purple (Figure 5b). Since the thickness (10−20 nm estimated from the HRTEM and FESEM images) of the nano-CdS covering on the feather surface is not comparable with visible light wavelength, such nano-CdS covering has little relationship with PhCs and should act as normal CdS in the reflection spectrum. However, the reflection spectrum of the nano-CdS/red barb hybrid (sample ED-RT) does not match well with the simple accumulation of the signals from normal CdS and the original red barb. This phenomenon implies that the color change should not be simply caused by the nano-CdS covering on the feather surface but be highly due to the change of the photonic band structure of the 2D PhCs beneath the feather surface. By consideration that the refractive index of CdS (ranges from 2.5 to 2.3 for wavelength between 400 and 800 nm)[23] is not approximative to that of the connecting keratin (1.54) and differs from that of the melanin

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rods (2.0)[12] within peacock feathers, the introduction of nano-CdS into the PhCs (on melanin rods) will influence the periodic dielectric structure and change the photonic band structure. Therefore, the incorporation of nano-CdS inside the 2D PhCs within peacock feathers results in a modification of the photonic band structure, as well as creates novel hybrids PhCs.

Conclusion

In summary, an approach has been demonstrated to be effective to incorporate cubic CdS nanocrystallites in the natural 2D photonic crystals (PhCs) within peacock feathers. The optimal process was investigated to fix on the procedure involving the introduction of active COO^- groups to the keratin component of peacock feathers by the EDTA/DMF activation as well as the in situ synthesis of suitable amount of CdS seeds on the active COO^- groups, followed by the solvothermal procedure to further gain nano-CdS. In the final nano-CdS/feathers hybrids, nano-CdS (5−6 nm) assemble into small wormlike aggregations that distribute well both on the feather surface and inside the 2D PhCs. And the efficient loading of nano-CdS results in novel hybrids PhCs with different photonic band structure from that of the natural PhCs within original feathers. This strategy provides opportunities for applying natural PhCs in the fabrication of modern optoelectronic devices.

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Supporting Information Available: FESEM images of control samples and the illustration of related mechanism. This material is available free of charge via the Internet at http://pubs.acs.org.

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